

Thermodynamics of the superconducting state in Calcium at 200 GPa

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The thermodynamic parameters of the superconducting state in Calcium under the pressure at 200 GPa were calculated. The Coulomb pseudopotential values (μ^*) from 0.1 to 0.3 were taken into consideration. It has been shown, that the specific heat's jump at the critical temperature and the thermodynamic critical field near zero Kelvin strongly decrease with μ^* . The dimensionless ratios $r_1 \equiv \Delta C(T_C)/C^N(T_C)$ and $r_2 \equiv T_C C^N(T_C)/H_C^2(0)$ significantly differ from the predictions based on the BCS model. In particular, r_1 decreases from 2.64 to 1.97 with the Coulomb pseudopotential; whereas r_2 increases from 0.140 to 0.157. The numerical results have been supplemented by the analytical approach.

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I. INTRODUCTION

By using the advanced technique, it is experimentally possible to explore the properties of the superconducting state under the high pressure (p). In particular, the above researches enable: (i) the test of the theories for the superconducting state, (ii) as well as to improve the properties of the superconductors, and (iii) to create the new superconductors. At present, the 52 elemental superconductors are known, however 22 of them superconduct if the pressure is applied [1]. The most interesting elements are: Lithium, where the critical temperature (T_C) rises rapidly to ~ 14 K at 30.2 GPa [2], Yttrium with the maximum value of the critical temperature of 20 K at 115 GPa [3], and Calcium which has the highest observed value of T_C (25 K at 161 GPa) [4], [5], [6].

The thermodynamic properties of the superconductors under the high pressure can be analyzed in the framework of the Eliashberg approach [7], [8], [9]. In this formalism the complicated form of the electron-phonon interaction is modeled by Eliashberg function ($\alpha^2 F(\Omega)$). We notice that the first-principle calculations of $\alpha^2 F(\Omega)$ require the knowledge of the electronic wave functions, the phonon spectrum, and the electron-phonon matrix elements between two single-electron Bloch states. Experimentally, the form of the Eliashberg function can be directly obtained from the second derivative of I - V curve for the tunnel junction ($d^2 V/dI^2 \sim \alpha^2 F(mV)$) [10].

From the physical point of view, the Eliashberg approach represents particularly important method of the analysis, since it enables the calculation of the thermodynamic parameters on the quantitative level. In particular, the exact form of the free energy difference between the superconducting and normal state should be calculated on the basis of the so-called Eliashberg equations [11]. In the considered case, the input parameters are the Eliashberg function and the Coulomb pseudopotential (μ^*), where μ^* models the Coulomb repulsion between electrons. We notice that its value is selected in such way that T_C determined on the basis of the Eliashberg equations equals the experimental value of the critical temperature.

In the presented paper, we have analysed the thermodynamic properties of Calcium under the pressure at 200 GPa by using the Eliashberg approach. In particular, the following parameters were taken into account: the specific heat in the superconducting state (C^S), the specific heat in the normal state (C^N), and the thermodynamic critical field (H_C). Additionally, the dimensionless ratios $r_1 \equiv (C^S(T_C) - C^N(T_C))/C^N(T_C)$ and $r_2 \equiv T_C C^N(T_C)/H_C^2(0)$ have been determined [12].

For Calcium, the dependence of the critical temperature on the pressure has been obtained experimentally by Okada *et al.* in 1996 [5] and then by Yabuuchi *et al.* in 2006 [4]. The results prove that the critical temperature grows with the pressure from the value of about 1 K ($p = 50$ GPa) to 25 K ($p = 161$ GPa). On the basis of the Yabuuchi's results it is easy to show that the values of the Coulomb pseudopotential can be large. For example, $[\mu^*]_{p=120\text{GPa}} = 0.215$ and $[\mu^*]_{p=160\text{GPa}} = 0.241$ [13], [14]. In the case of the pressure 200 GPa, the experimental value of T_C is still unknown, therefore the wide range of the Coulomb pseudopotential's values have been considered in the paper; $\mu^* \in \langle 0.1, 0.3 \rangle$.

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II. THE ELIASHBERG EQUATIONS

The Eliashberg functions for Calcium were determined by Yin *et al.* [6]. At the pressure 200 GPa, the *Pnma* structure is clearly favored, and the linear-response calculations indicate that it is also dynamically stable. Additionally, the Yin's results have shown that the strong electron-phonon coupling persists and T_C can be high (~ 30 K). In the paper, the thermodynamic parameters for Calcium have been calculated by using the Eliashberg equations on the imaginary axis, the Yin's Eliashberg function has been taken into account.

The Eliashberg set has the following form:

$$Z_n = 1 + \frac{1}{\omega_n} \frac{\pi}{\beta} \sum_{m=-M}^M \lambda(i\omega_n - i\omega_m) \frac{\omega_m Z_m}{\sqrt{\omega_m^2 Z_m^2 + \phi_m^2}}, \quad (1)$$

and

$$\phi_n = \frac{\pi}{\beta} \sum_{m=-M}^M [\lambda(i\omega_n - i\omega_m) - \mu^* \theta(\omega_c - |\omega_m|)] \frac{\phi_m}{\sqrt{\omega_m^2 Z_m^2 + \phi_m^2}}. \quad (2)$$

The wave function renormalization factor is denoted by $Z_n \equiv Z(i\omega_n)$, and the order parameter function by $\phi_n \equiv \phi(i\omega_n)$. The n -th Matsubara frequency has the form: $\omega_n \equiv (\pi/\beta)(2n-1)$, where $\beta \equiv (k_B T)^{-1}$ and k_B is the Boltzmann constant. We notice that the value of the order parameter is given by the ratio: $\Delta_n \equiv \phi_n/Z_n$. In Eqs. (1) and (2) the symbol $\lambda(z)$ denotes the electron-phonon pairing kernel:

$$\lambda(z) \equiv 2 \int_0^{\Omega_{\max}} d\Omega \frac{\Omega}{\Omega^2 - z^2} \alpha^2 F(\Omega), \quad (3)$$

where the maximum phonon frequency Ω_{\max} is equal to 78.1 meV. Finally, θ denotes the Heaviside unit function and ω_c is the cut-off frequency ($\omega_c = 3\Omega_{\max}$).

From the mathematical point of view the exact solution of the Eliashberg equations represents a complicated problem. We notice that formally the Eliashberg set contains the infinite number of the non-linear algebraic equations; in addition every equation has the integral kernel, which is dependent on the form of the Eliashberg function. It is possible to prove, that if we limit the number of the Matsubara frequencies, the solutions of the Eliashberg equations lose the convergence only in the area of the very low temperatures. In the paper we assume $M = 1100$. In this case the functions Z_n and ϕ_n are stable for $T \geq 3.48$ K. The Eliashberg equations have been solved by using iterative method [15].

III. THE NUMERICAL RESULTS

In Fig. 1 the order parameter as a function of the number m has been presented. We have considered the selected values of the Coulomb pseudopotential and temperatures. It is easy to see that Δ_m decreases with m number's growth. In particular, the strong fall of the order parameter appears for low values of m ; for higher values the function Δ_m saturates. Very similar dependence on the number m possesses the wave function renormalization factor (see Fig. 2). However, the function Z_m saturates considerably slower than Δ_m .

The growth of the Coulomb pseudopotential's value differently influences on the order parameter and the wave function renormalization factor. In the first case the values of the order parameter strongly decrease; whereas the function Z_m is practically not changing. From the physical point of view the above facts mean, that together with the increasing of μ^* decreases only the value of the critical temperature; the electron effective mass remains fixed ($m_e^* \sim Z_{m=1}$).

The solutions of the Eliashberg equations also very unlikely evolve with the temperature. Most clearly this fact is possible to observe in Fig. 3, where the dependences of $\Delta_{m=1}$ and $Z_{m=1}$ on the temperature have been plotted. In particular, the obtained results show that the temperature dependence of the order parameter can be modeled by the function: $\Delta_{m=1}(T) = \Delta_{m=1}(0) \sqrt{1 - \left(\frac{T}{T_C}\right)^\beta}$, where the parameters $\Delta_{m=1}(0)$, T_C , and β are collected in Tab. I. On the other hand, the wave function renormalization factor is slightly depended on the temperature.

In order to obtain the specific heats and the thermodynamic critical field, we have to calculate the free energy difference between the superconducting and normal state (ΔF) [11]:

$$\frac{\Delta F}{\rho(0)} = -\frac{2\pi}{\beta} \sum_{m=1}^M \left(\sqrt{\omega_m^2 + \Delta_m^2} - |\omega_m| \right) \left(Z_m^S - Z_m^N \frac{|\omega_m|}{\sqrt{\omega_m^2 + \Delta_m^2}} \right). \quad (4)$$

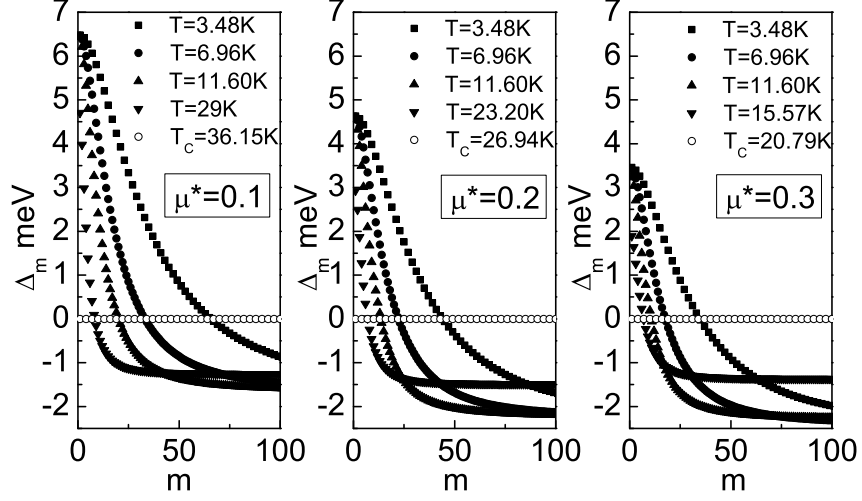


FIG. 1: The dependence of the order parameter on m for selected values of the Coulomb pseudopotential and temperatures.

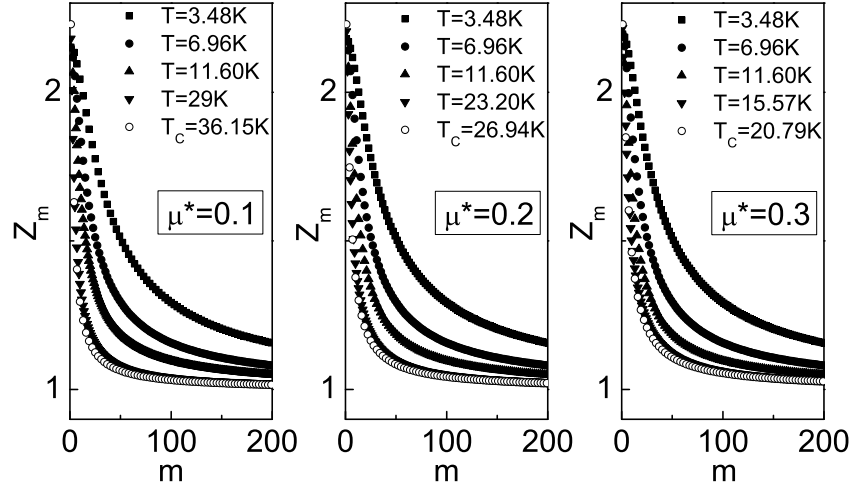


FIG. 2: The dependence of the wave function renormalization factor on m for selected values of the Coulomb pseudopotential and temperatures.

The functions Z_m^S and Z_m^N represent the wave function renormalization factors for the superconducting (S) and normal (N) state respectively.

The specific heat difference between the superconducting and normal state ($\Delta C \equiv C^S - C^N$) can be obtained by

TABLE I: The values of $\Delta_{m=1}(0)$, T_C , and β parameters.

μ_C^*	$\Delta_{m=1}(0)$ meV	T_C K	β
0.1	6.48	36.15	3.47
0.2	4.63	26.94	3.50
0.3	3.45	20.79	3.60

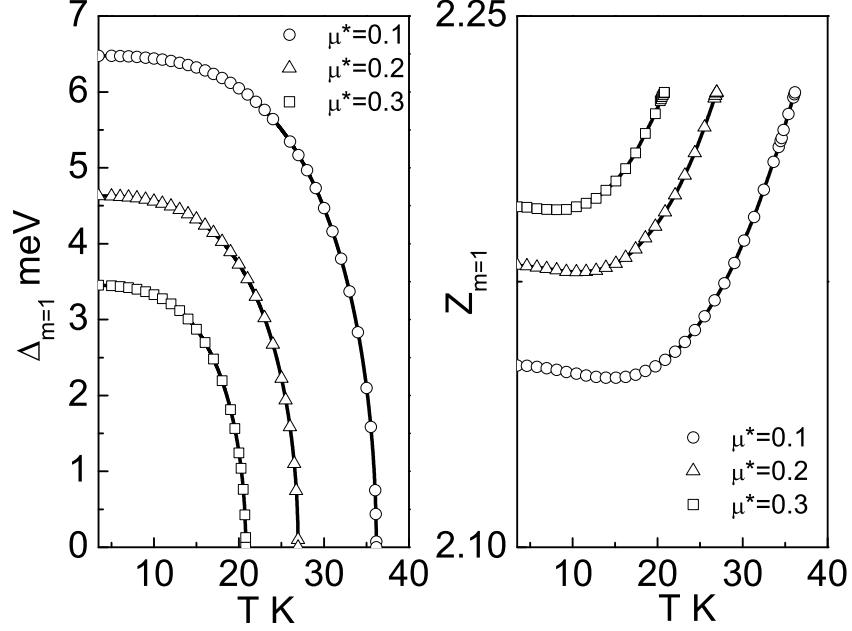


FIG. 3: The dependence of the order parameter and the wave function renormalization factor on the temperature for selected values of the Coulomb pseudopotential. In both cases we assume $m = 1$.

using the expression:

$$\frac{\Delta C}{k_B \rho(0)} = -\frac{1}{\beta} \frac{d^2 [\Delta F / \rho(0)]}{d(k_B T)^2}. \quad (5)$$

On the other hand, the specific heat in normal state is given as:

$$\frac{C^N}{k_B \rho(0)} = \frac{\gamma}{\beta}, \quad (6)$$

where $\gamma \equiv \frac{2}{3}\pi^2(1 + \lambda)$. In Fig. 4 the specific heat for the superconducting and normal state as a function of the temperature has been shown. It is easy to see that the specific heat's jump at the critical temperature decreases with the growth of the Coulomb pseudopotential. In particular, $\left[\frac{\Delta C(T_C)}{\rho(0)} \right]_{\mu^*=0.3} / \left[\frac{\Delta C(T_C)}{\rho(0)} \right]_{\mu^*=0.1} \simeq 0.43$.

The thermodynamic critical field has been calculated by using the formula:

$$\frac{H_C}{\sqrt{\rho(0)}} = \sqrt{-8\pi [\Delta F / \rho(0)]}. \quad (7)$$

In Fig. 5 the dependence of $H_C / \sqrt{\rho(0)}$ on the temperature has been presented. We can see, that the value of the thermodynamic critical field near the temperature of zero Kelvin ($H_C(0) \simeq H_C(T_0)$) also strongly decreases with μ^* ; $\left[\frac{H_C(0)}{\sqrt{\rho(0)}} \right]_{\mu^*=0.3} / \left[\frac{H_C(0)}{\sqrt{\rho(0)}} \right]_{\mu^*=0.1} \simeq 0.55$.

The dimensionless ratios r_1 and r_2 on the basis of the calculated thermodynamic functions have been determined. We notice that in the framework of the BCS model these parameters have the universal values: $[r_1]_{\text{BCS}} = 1.43$ and $[r_2]_{\text{BCS}} = 0.168$ [12]. For Calcium the theoretical data have been collected in Fig. 6. We see that even for large values of μ^* the ratios significantly diverge from the values predicted by the BCS model. Below, we have given the formulas, which enable the simple calculations of r_1 and r_2 . In particular:

$$\frac{r_1}{[r_1]_{\text{BCS}}} = 1 - 42.5 \left[\left(\frac{f_1}{f_2} \frac{k_B T_C}{\omega_{\text{ln}}} \right)^2 \ln \left(\frac{3}{2} \frac{f_1}{f_2} \frac{k_B T_C}{\omega_{\text{ln}}} \right) \right], \quad (8)$$

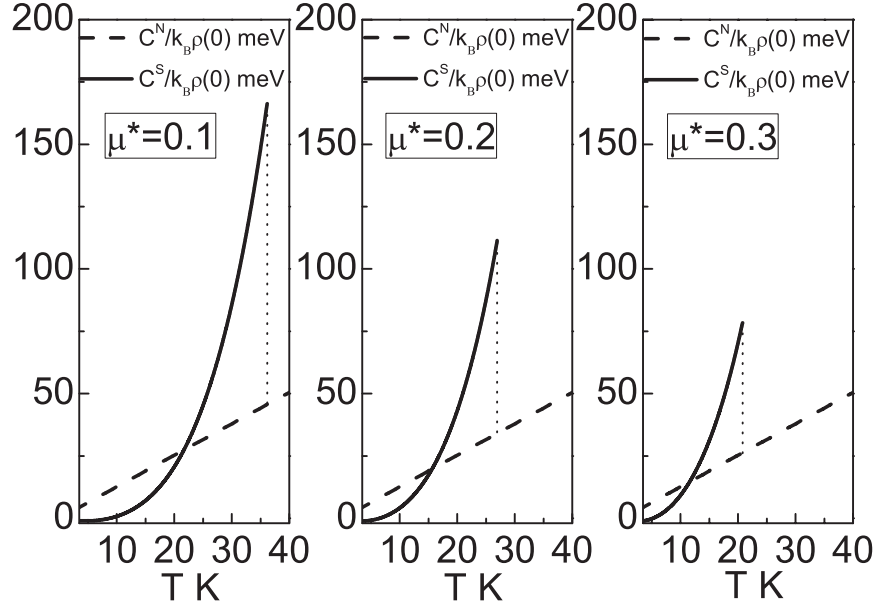


FIG. 4: The dependence of the specific heat in the superconducting and normal state on the temperature for selected values of the Coulomb pseudopotential. The vertical line indicates the position of specific heat's jump that occurs at T_C .

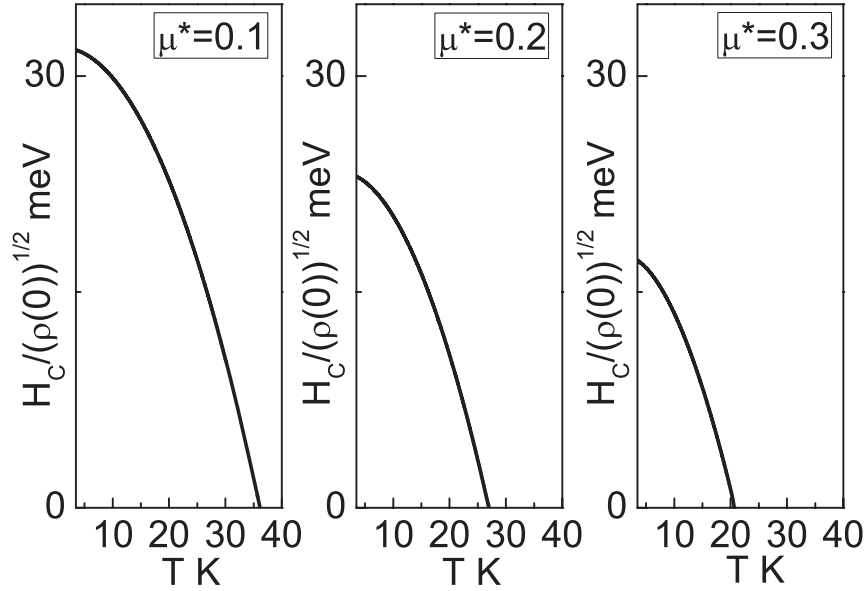


FIG. 5: The thermodynamic critical field as a function of the temperature for selected values of the Coulomb pseudopotential.

and

$$\frac{r_2}{[r_2]_{\text{BCS}}} = 1 + 2.7 \left[\left(\frac{f_1}{f_2} \frac{k_B T_C}{\omega_{\text{ln}}} \right)^2 \ln \left(\frac{1}{33} \frac{f_1}{f_2} \frac{k_B T_C}{\omega_{\text{ln}}} \right) \right]. \quad (9)$$

We notice that the numerical coefficients in Eqs. (8) and (9) by the least-squares analysis of 60 exact r_1 and r_2 values have been chosen. Finally, the critical temperature by using the *modified* Allen-Dynes formula should be calculated [16]:

$$k_B T_C = f_1 f_2 \frac{\omega_{\text{ln}}}{1.45} \exp \left[\frac{-1.03 (1 + \lambda)}{\lambda - \mu^* (1 + 0.06 \lambda)} \right], \quad (10)$$

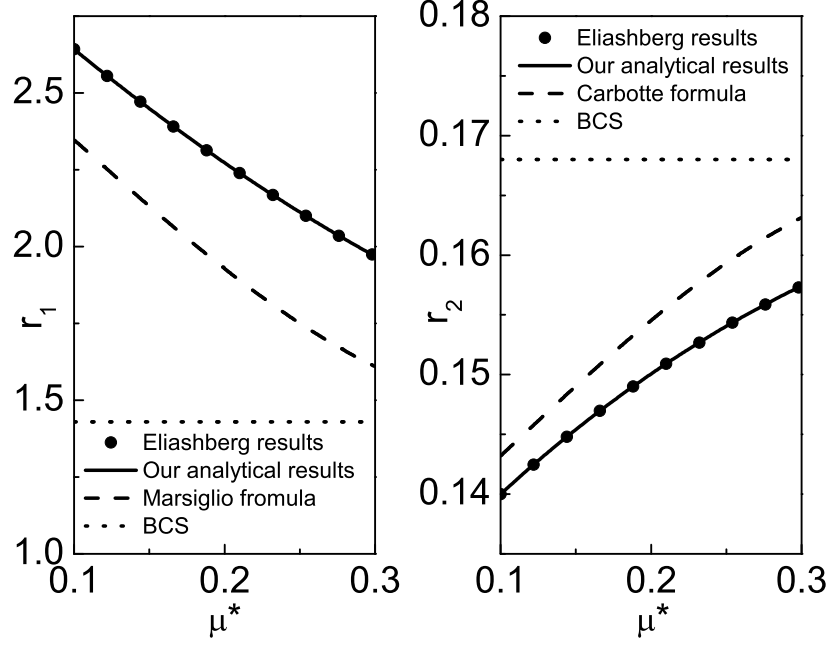


FIG. 6: The ratios r_1 and r_2 as a functions of the Coulomb pseudopotential. The black circles show the exact results obtained on the basis of the Eliashberg equations. The solid lines represent the calculation of the r_1 and r_2 parameters using our analytical scheme (Eq. (8) and Eq. (9)). The dashed lines represent the results obtained in the framework of the Marsiglio [8] and Carbotte [9] formulas respectively. The dotted lines denote the BCS values.

where the strong-coupling correction function (f_1) and the shape correction function (f_2) are given by:

$$f_1 \equiv \left[1 + \left(\frac{\lambda}{\Lambda_1} \right)^{\frac{3}{2}} \right]^{\frac{1}{3}}, \quad (11)$$

and

$$f_2 \equiv 1 + \frac{\left(\frac{\sqrt{\omega_2}}{\omega_{\text{ln}}} - 1 \right) \lambda^2}{\lambda^2 + \Lambda_2^2}. \quad (12)$$

The functions Λ_1 and Λ_2 have the form:

$$\Lambda_1 \equiv 2.6 (1 + 1.8\mu^*), \quad (13)$$

and

$$\Lambda_2 \equiv 0.092 (1 - 150\mu^*) \left(\frac{\sqrt{\omega_2}}{\omega_{\text{ln}}} \right). \quad (14)$$

The parameter ω_2 is the second moment of the normalized weight function, ω_{ln} denotes the logarithmic phonon frequency and λ is called the electron-phonon coupling constant. In the case of Calcium under the pressure at 200 GPa the following results have been obtained: $\sqrt{\omega_2} = 35.92$ meV, $\omega_{\text{ln}} = 29.98$ meV and $\lambda = 1.228$.

IV. SUMMARY

The thermodynamic parameters of the superconducting state in Calcium under the pressure at 200 GPa have been analyzed in the paper. The numerical calculations in the framework of the Eliashberg approach have been made. On the basis of the exact Eliashberg solutions the specific heats and the thermodynamic critical field have been determined.

For the wide range of the Coulomb pseudopotential values ($\mu^* \in \langle 0.1, 0.3 \rangle$), it has been shown that the specific heat's jump at the critical temperature and the thermodynamic critical field near zero Kelvin strongly decrease with μ^* .

The dimensionless ratios r_1 and r_2 significantly differ from the predictions based on the BCS model even for high values of the Coulomb pseudopotential. In particular, $r_1 \in \langle 2.64, 1.97 \rangle$ and $r_2 \in \langle 0.140, 0.157 \rangle$.

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